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AN AUTOMATED PROCESS FOR GENERATION OF NEW FUEL BREAKDOWN MECHANISMS

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SUMMARY/OVERVIEW:

This work revolves around an innovative, comprehensive, and integrated approach for predicting new fuel reaction mechanisms. It combines advanced computational techniques in a synergistic study of the critical processes in fuel decomposition at a level of detail that can help distinguish, correct, and quantify mechanisms for these processes. The innovative aspect of the modeling effort is to integrate computational tools that can be used to build reaction pathways for new fuel mechanisms, starting from the structure of the proposed fuel components and ending with a list of reactions pathways, rate constants, thermodynamic, and transport data that can be feed into existing combustion mechanisms. This will be accomplished by using a combination of two well-defined techniques: Molecular Dynamics and ab initio electronic structure calculations.

While the efforts present in the literature are targeted to build kinetic mechanisms in terms of kinetic and thermochemical data often based on similarity or to gather data from different sources, they do not address the other main problem related to the reliability of reaction mechanisms, that is the exclusion of significant pathways from the list of the reactions that are included in the mechanisms. The approach presented in this proposal will allow the identification of new reaction pathways to produce a more complete description of the system of interest.

The final objective of this project is to convert the building of kinetic mechanisms into science, automate the methodology, and make the results available in a prompt and convenient form for the user. The project refers to automation in the sense that a rigorous process is proposed to go from fuel structure to kinetic mechanism without requiring the intervention of the investigator. One of the advantages is that it avoids the introduction of bias based on the preconceived notions of the community.

2. TECHNICAL DISCUSSION

When dealing with complex real fuels, surrogates are formulated and used in place of the real fuel both for experimental and computational applications. A surrogate is a mixture of a limited number of hydrocarbons with a well defined and reproducible composition that can be used in place of the real fuel. The use of a surrogate blend, comprised of a relatively small number of

high purity hydrocarbons blended to simulate the combustion performance of practical fuel, has the advantage of allowing fuel composition to be accurately controlled and monitored. In addition to providing a model fuel for the study of the effect of fuel properties and chemical composition on combustor performance, the compositional control afforded by a surrogate fuel is attractive for the development and verification of computational codes for combustor design or fire simulation.

The type of surrogate mixture used is dependent ideally upon the fuel properties that are being simulated: surrogates may be tailored to reproduce the physical, chemical, or more comprehensive behavior of a fuel in a given application. A physical surrogate can be designed to reproduce physical properties such as density, thermal conductivity, heat capacity, viscosity, surface tension, and volatility. A chemical surrogate, on the other hand, has similar hydrocarbon types and distribution, and can reproduce chemical properties such as oxidation stability, ignition temperature, rates of reaction, sooting behavior. As an example, for JP-8 pool fires the relevant properties include volatility (boiling range, flash point, vapor pressure), chemical kinetics (particularly of reactions leading to soot formation, needed for accurate simulation of radiative heat transfer in fires) and other combustion properties such as ignition, peak heat release rate and local flame extinction.

Usually surrogates match only some particular aspects of the behavior of the real fuel. And new formulations are frequently proposed to improve their capabilities and to expand the number of properties they reproduce. As a consequence, there is a continuing need for additional kinetic mechanisms to cover the chemistry of new species and/or new conditions. The problem is that when new species are introduced in the surrogate, there is no good method for updating the kinetic mechanism to incorporate the new species.

The approach presented below makes it possible to identify new reaction pathways for real fuels to produce a complete description of the system of interest in terms of intermediates, products, kinetics, thermochemical and transport properties.

Below we report on the new approach that can be taken to *generate new fuel mechanisms*. This process utilizes an Accelerate Molecular Dynamics methodology to identify reaction pathways at relevant temperatures in conjunction with *ab initio* calculations to determine the rates of new reactions. The approach allows the identification of new gas phase products and reaction pathways for new fuel mechanisms, starting from the structure of the proposed fuel components and ending with a list of reaction pathways, rate constants, and thermodynamic data.

2.1 COMPUTATIONAL METHODOLOGY

Two combined steps are required for these calculations. The first one is represented by an accelerated MD simulation that is used to evaluate alternative/additional reaction pathways for molecular systems with many conformational degrees of freedom, and quantum chemistry runs to validate the results obtained by the MD code.

Step 1: The input to Step 1 is the structure of the fuel compound. The Parallel Replica Molecular Dynamics (PRMD)¹ code is used to extend the MD simulation time in an accurate way. In the PRMD method, starting with an N atom system in a particular state, the system is replicated on many processors. After a dephasing stage, where momenta are randomized, each processor carries out an independent Molecular Dynamics trajectory. Whenever a structural transition is detected on any processor, all processors are alerted to stop. The simulation clock is advanced by the accumulated trajectory time summed all over replicas, and the PR simulation is restarted, continuing onward until the next transition occurs and the process is repeated. In this way, the effective time of the MD simulation is “boosted” (usually significantly).²

In summary:

Input to Step 1: the user defines the fuel structure

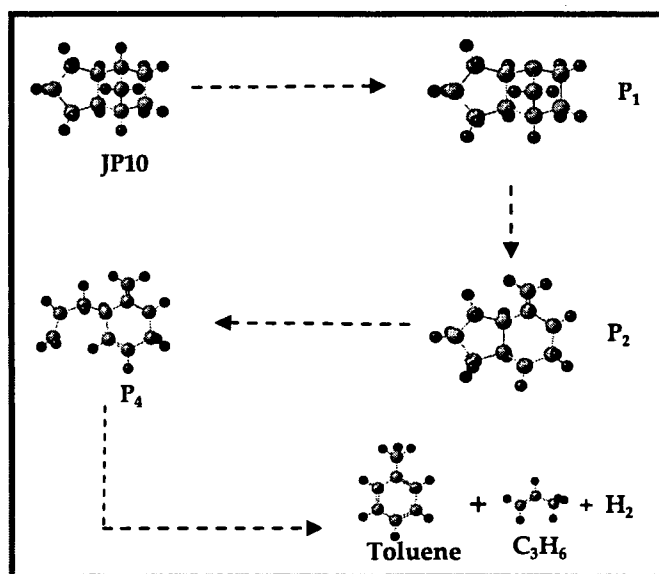
Outputs from Step 1: reaction pathways and products $P_{i,j}$ – the first index refers to the identity of the product within a particular pathway and the second to the identity of the reaction pathway. For example $P_{2,1}$ is the second product identified in pathway 1.

Step 2: The new reaction pathways identified with the PRMD code – in *Step 1* – will be validated and further studied using *ab initio* methods to determine kinetic and thermodynamic properties of the new routes. An essential requirement to build reliable kinetic mechanism is the availability of accurate kinetic parameters. Even small uncertainties in rate parameters may induce substantial deviations in model predictions of soot yields due to the accumulation of errors in the large number of growth steps necessary for the description of large compounds.

2.2 RESULTS

In order to emphasize the importance of this new methodology preliminary results have been obtained for JP10 fuel, whose mechanism is not well understood. The kinetic mechanism available in the literature for JP10³ includes a few reactions leading to C_3H_3 , C_2H_4 , C_5H_8 , C_2H_2 , C_4H_6 , C_3H_5 , but recent experimental data reported on JP10 pyrolysis show the presence of benzene, toluene, cyclopentadiene as initial decomposition products in a temperature range between 900 – 1300K.⁴

Using the approach reported above, Step 1 and Step 2 were applied to the JP10 molecule in a pyrolytic environment at a temperature of 1500 K. As input to the process, the structure of the JP10 molecule was defined. The next figure shows an example of the results obtained after Step 1. In the example showed in the figure, the run stops when the species produced are previously known and exist in large scale mechanisms. In this case toluene, C_3H_6 and H_2 . After Step 1 the



Example of output from Step 1: intermediates and products identified with PRD.

first reaction pathway and the intermediates are identified. This information is used as input for

the *ab initio* calculations and after Step 2 the reaction pathway is completed and the transition states calculated.

The results obtained through the use of the computational tool described above can be integrated into a hierarchically constructed kinetic model already available for the oxidation of alkanes and simple aromatic molecules (benzene, toluene, ethylbenzene, xylene etc.).⁵

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